

Experiments on the Interface between Germanium and an Electrolyte

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Measurements have been made of the electrode potential of p- and n-type germanium in contact with aqueous solutions of KOH, KCl and HCl as a function of anodic and cathodic current and of incident light intensity. For anodic currents, the measured electrode potential can be separated into three parts: the reversible electrode potential corresponding to the anodic reaction, depending only on the solution; an overvoltage of the usual form; and a term $(kT/e) \ln (p_1/p)$, where p is the equilibrium hole concentration and p_1 is the concentration just inside the space-charge region of the germanium. The anodic current is determined by flow of holes to the surface, so that the current saturates for n-type germanium but not for p-type. The saturation current is determined by body and surface generation of holes and by creation of excess holes by light. There is a current gain of 1.4 to 1.8. In addition, there is a small "leakage" current not dependent on hole supply. Similar statements may be made for cathodic current, except that the electrode potential and current are determined respectively by the concentration and supply of electrons instead of holes, the current gain is of the order of unity, and the leakage current is larger. Complicating time changes were observed for cathodic but not for anodic currents. The measurements may be understood in terms of simple thermodynamic considerations, based on the idea that the anodic reaction is with holes, the cathodic reaction with electrons, in the semiconductor; the behavior for very small currents depends on a competition between the anodic and cathodic reactions, which may be treated by simple rate process considerations. A comparison is made with experiments on the germanium-gas interface by Brattain and Bardcn, to which similar considerations may apply.

A. SURVEY OF THE WORK

1. INTRODUCTION

This paper reports studies of germanium electrodes in contact with aqueous electrolytes. Measurements have been made of electrode po-

tentials for germanium electrodes in contact with aqueous solutions of potassium hydroxide, potassium chloride and hydrochloric acid. Measurements were made as a function of anode or cathode current and also of light intensity. In one series of experiments with n-type germanium simultaneous measurements were made of changes in the density of the minority carriers, i.e., holes.

The measured half cell potentials may be understood in terms of the following conclusions. At a germanium anode, the primary reaction is with holes in the semiconductor and not with electrons.¹ Because of the long lifetime of minority carriers in high purity germanium, one can establish a steady (quasi-equilibrium) state in which the density of minority carriers may differ by many orders of magnitude in either direction from the equilibrium value. One way in which this may be done is to illuminate the surface. Illumination of the surface creates equal numbers of holes and electrons. The effect upon the density of majority carriers is not very large but the relative change in the density of minority carriers may be considerable. It is found that the effect of light on the electrode potential for a p-type germanium anode is rather small, but that for n-type the effect is large. The electrode potential is found to depend upon the concentration of holes in the way which one would expect from thermodynamics if the holes are taking part as one of the components in the anodic process. From this we conclude that the primary reaction at a germanium anode is with holes. Physically the primary process in oxidation must be the transfer of the electron from the electrolyte into the valence band of the semiconductor. It has been found however that the current flowing is larger than the flow of holes by a factor of the order of 1.6. This seems to indicate that once one electron has been transferred from the electrolyte a further transfer of charge, this time into the conduction band, can take place. This gives rise to a current multiplication which one may compare with the current multiplication occurring at the collector of a point contact transistor.

At a germanium cathode the situation is complicated by time effects. In some solutions these are relatively unimportant or are confined to a particular range of electrode potential; in other solutions it is difficult to get reproducible results at all. In general it is found, however, that the primary reaction occurring on first switching on the current is with electrons rather than with holes. The evidence for this is the fact that the electrode potential for cathodic current is found initially to depend in the same way on electron concentration as does the electrode potential for anode current on hole concentration.

The experiments also give information as to the rapidity with which

minority carriers can recombine at the interface. Note that this process is quite distinct from the flow of carriers across the surface (See Appendix 1). The surface recombination velocity does not seem to vary much with the current crossing the surface, and is of the same order of magnitude as for a dry germanium surface which has been given an oxidizing etch and left in a neutral gas environment.

The change-over from anodic to cathodic process takes place near zero current and may be studied by observing the change from positive to negative surface photo-effect. From these measurements one may make tentative conclusions as to the form of the over-voltage and the equilibrium potential for the anode and cathode reactions. Unfortunately, these experiments do not give any insight as to the nature of the anodic and cathodic processes other than the part played in them by the carriers in the two energy bands in the semiconductor. Likewise no information is obtained as to the location of charge in the surface of the semiconductor. It is not possible to say how much of this charge resides in the comparatively wide space-charge region at the semiconductor surface and how much is located in surface states. The reason for this is that the quantities measured in the experiment may be related one to another by purely thermodynamical considerations.

2. HISTORY

It is an almost invariable rule that at any interface between two phases there is a separation of charge forming a space-charge double layer. This is of particular interest at a semiconductor surface because the space charge region extends relatively far (of the order of 10^{-4} cm.) into the semiconductor. The space charge region at the surface of a semiconductor is of great importance in semiconductor technology. A simple theory for the space charge region at the surface of a semiconductor was proposed some years ago by Mott² and by Schottky.³ There are some features of the space-charge region which are still somewhat of a mystery, however. From the simple theory one would predict that the application of a strong electric field normal to the surface should change the conductivity of the semiconductor. This change in surface conductivity has been found, but is smaller by about an order of magnitude than one would predict.⁴ This observation can be understood if one supposes that the interior is shielded by "surface states" of the type proposed by Bardeen.⁵ One might suppose that the existence of these surface states could be confirmed by the type of experiment in which one measured

some sort of "surface potential", viz. a measured potential difference between two phases, one of which is the semiconductor.

One such study has been made by Brattain and Bardeen.⁶ In these experiments the authors measured the contact potential and surface photo-effect for a germanium surface exposed to various gases. Now any such germanium surface must be covered by a layer of charged particles viz., ions, and such a layer of charged particles is accompanied by a field normal to the surface. One would therefore expect that by changing the gas environment, and therefore the magnitude and possibly the sign of the adsorbed ionic charge, one could alter the contact potential and the magnitude and sign of the surface photo-effect. These measurements show such changes and were interpreted in terms of a particular model of surface states. Other interpretations are however possible.⁷ In view of the rather considerable complexity of the Brattain-Bardeen surface states model, one would like to have independent evidence as to its validity. Specifically, it would be advantageous to proceed further into the extremes of surface potential in order to determine the exact location in energy of the postulated surface states. The experiments to be reported in this paper were originally undertaken with this aim in view.

There is another way in which one may change the sign and magnitude of an ionic surface charge on the surface of a semiconductor. This is to make the semiconductor one electrode of an electrolytic cell. By changing the magnitude and sign of the cell current, one should be able to change the nature of the ion layer near the germanium surface. Some qualitative experiments of this type were reported by one of us (WHB) some years ago.⁸ The experiments were carried out with silicon. The surface photo effect, first found with a silver chloride electrode by Becquerel,⁹ was measured, and was found to depend very sharply on the current flowing. The reason for the existence of a surface photo-effect may be thought of as follows. Suppose that no net current is crossing the surface. In the dark the rates of flow of electrons and of holes to and from the surface will all be the same. When the surface is illuminated this balance is upset; the surface potential must then re-adjust itself in such a way that the net flow of electrons to the surface is equal to the net flow of holes to the surface. For a given intensity of illumination, these two rates will be the higher, the higher the surface recombination velocity. It therefore follows that a high surface recombination velocity would give rise to a low surface photo-effect and vice versa. At the time these experiments were done, a qualitative interpretation was given in terms of an analogy with a rectifier. The object of the present work was more

completely to understand the semiconductor-electrolyte system, and, if possible, to extend the experiments done on the germanium-gas system to the condition in which the change in surface potential is so large that the exact location of the surface states may be determined. As has been stated above, the latter hope has not been fulfilled.

3. PLAN OF THE PAPER

In the next paragraph an outline of the experiments is given. Most of the experiments have been carried out with blocks of germanium so large that every dimension is great in comparison with the minority carrier diffusion length. These are reported in Section B. Experiments designed to study the changes in minority carrier density are described in Section C. The conclusions to the experiments described in this paper are given in Sections D and E.

4. OUTLINE OF THE EXPERIMENT

Standard electro-chemical methods¹⁰ have been used to measure electrode potential with light as an additional variable. The electrode potential for p-type and n-type germanium in contact with various solutions has been measured in light of a series of known intensities.

The surface photo effect is defined by the quantity $(dV^E/dL)_{I_E}$, where L is defined as the number of hole-electron pairs created per second per unit area, multiplied by e , the electronic charge. This is the maximum photo-current which would pass if every minority carrier were collected (See Appendix 1). This quantity may be derived from the dc measurements; it is however convenient to make an independent measure of it on an ac basis. This measurement will be reliable provided that there is no dispersion between zero frequency and the frequency used for the ac experiment.

It soon became apparent that p-type and n-type germanium behave very differently; n-type germanium shows a large positive surface photo-voltage for anodic current and a small negative photo-voltage when the current is cathodic; for p-type germanium the sign of the photo-voltage is correlated with the sense of the current in the same way, but the relative magnitudes are reversed. The measurements on n-type germanium showed a sharp saturation of anodic current, the value at which saturation occurred depending on the intensity of illumination of the surface. A similar saturation was found in cathodic current for p-type germanium, although in this case the saturation was less sharp. It was suspected that these effects might be due to the exhaustion of minority

carriers. It therefore became important to have some independent means for following changes in the minority carrier density just inside the space charge region.

Fortunately, the minority carrier diffusion length in germanium is quite long. It is therefore possible to make electrochemical measurements on one side of a thin slice of germanium and measurements of minority carrier density on the other. Experiments of this type have been carried out with n-type slices of the order of 10^{-2} cm. in thickness — a distance large in comparison with the thickness of the space charge region but still small in comparison with a minority carrier diffusion length. The back surface is covered with a large-area rectifying junction. From measurements of the floating potential across this junction one calculates the hole density near the back surface. The value of the hole density near the electrolyte surface may then be deduced. Since the slice is thin in comparison with a diffusion length, these two densities will not usually be very different.

The rectifying junction at the back of the thin slice has another use. As an alternative to creating surplus holes by shining light on the electrolyte surface, it is also possible to inject them by passing a positive current from the alloyed region into the semiconductor. This gives us a way of calibrating the intensity of the light. Thus one can measure the floating potential at the rectifying contact, the electrode potential and the ac surface photo effect as functions of electrolyte current, current across the rectifying barrier and light intensity. These experiments have shown that, at anode current I^E , the electrode potential V^E is given by the following equation:*

*The sign convention used in this paper for electrode current and electrode potential is explained in the table given below:

Voltage		Current	
Plus	Minus	Plus	Minus
Less noble	More noble	Cathodic	Anodic

The convention for currents agrees with that common in semiconductor physics (conventional current *into* the semiconductor positive); the convention for voltages agrees with that of the American Chemical Society, but disagrees with that of the American Electrochemical Society and of European electrochemists. Electrode voltages are given with respect to the particular standard electrode used by us (silver-silver oxide in N/10 KOH); to convert to the normal hydrogen electrode, subtract 0.41 volts.

The words "cathodic" and "anodic" also require explanation. That sense of current is called anodic which tends to promote an oxidative reaction at the electrode surface; the other sense is cathodic. At and near zero current, however, both oxidative and reductive processes will be going on at the time; thus, if we use the terms anodic and cathodic to distinguish oxidative and reductive *reactions* as well as to describe the two senses of external current, we have the paradox that both anodic and cathodic processes are occurring at all times, whether the external current is anodic or cathodic — though one process will greatly predominate whenever the net current is at all large. (See Section D.)

$$V^E = V_{0A}^E - \frac{K_A}{\beta} \ln \left(1 + \frac{|I^E|}{I_{0A}^E} \right) + \frac{1}{\beta} \ln \frac{p_1}{p} + I^E R_{\text{appr.}} \quad (1)$$

where $\beta = kT/e = 39 \text{ volts}^{-1}$.

In this equation the first term is an equilibrium potential V_{0A}^E for the anode, the second term is the ordinary Tafel¹¹ over-voltage; the third term shows how the electrode potential depends upon the concentration of the minority carriers and the fourth term represents the IR drop through any series resistance, such as the ohmic resistance of the germanium slice. The term which is of interest to us is the third. This may be regarded as part of the equilibrium* electrode potential, and shows that holes are one of the components in the primary anodic reaction.

If this is so, one would expect the anode current to depend upon the flow of holes up to the semiconductor surface. Let I_s be the saturation current for minority carriers, that is, the maximum rate at which they may come up to the surface from generation within the body or at the surface itself. The flow of holes up to the surface may then be related¹² to the concentration of holes just within the space charge region and the intensity of illumination by the following equation:

$$I_p = I_s \left(\frac{p_1}{p} - 1 \right) - L \quad (2)$$

which is analogous to a similar expression for a p-n junction. The experiments show that I^E and I_p can be related by writing:

$$I^E = \alpha I_p + \Delta \quad (3)$$

where α , the current gain for the surface is a constant and Δ is a small "leakage" current,¹³ a function only of V^E .

One may check equations (1), (2) and (3) from the measurements of surface photo-effect. From these equations one finds

$$\left(\frac{\partial L}{\partial V^E} \right)_{I^E} = \beta I_s \left(\frac{p_1}{p} \right) + \frac{1}{\alpha} \frac{d\Delta}{dV^E} \quad (4)$$

so that, for constant electrolyte current one should have, neglecting the second term of equation (4),

$$V^E = \frac{1}{\beta} \ln \left(\frac{\partial L}{\partial V^E} \right)_{I^E} + \text{const.} \quad (5)$$

* By imagining the rates of the various recombination processes to be vanishingly small, one may consider the disturbed (e.g., illuminated) condition of the germanium as a quasi-equilibrium state.

These measurements also enable one to find the quantity I_s , by determining the value of $(\partial L / \partial V^E)_{I^E}$ for which $p_1 = p$. There are various ways in which this may be done.

For p-type material, measurements have not yet been made with the thin slice technique. The information obtained from the experiments on the n-type slices, however, enables one to understand the experiments made on large blocks of either type. In this way, one may check equation (5) on p-type material in the cathode direction and so show that, by analogy with equation (1), the initial electrode potential for p-type material in the cathode direction is given by the equation:

$$V^E = V_{oc}^E + \frac{K_c}{\beta} \ln \left(1 + \frac{I^E}{I_{oc}^E} \right) - \frac{1}{\beta} \ln \frac{n_1}{n} + I^E R_{spr}. \quad (6)$$

Further, the current flowing is related to the light current L and the electron density n_1 just inside the space-charge region by the equations

$$\left. \begin{aligned} -I_n &= I_s \left(\frac{n_1}{n} - 1 \right) - L \\ I^E &= \alpha I_n + \Delta \end{aligned} \right\} \quad (7)$$

which are analogous to equations (2) and (3). The current gain α is different in the anode and cathode directions; the same is true for the dependence of the leakage current Δ on V^E . Otherwise the anodic properties of n-type germanium and the initial cathodic properties of p-type germanium are identical.

These considerations account for the behavior when the current is of that sense which gives a large photo-voltage. We shall show further that equations (1) and (6) describe also the small positive photo-voltage found for p-type germanium in the anode direction and for the small negative photo-voltage in the cathode direction on n-type. Holes are required for the anode process; it is more difficult to change the concentration of holes in p-type material than in n-type material, and therefore the measured electrode potential is less sensitive to light. A similar argument applies for electrons in n-type material. The change in phase of surface photo-voltage thus corresponds, qualitatively, to the changeover from anodic to cathodic processes. We shall return to this question in Section D. For the moment we are chiefly interested in the surface photo-effect as a means for determining minority carrier density for n-type material in the anode direction and for p-type material in the cathode direction.

B. EXPERIMENTS ON LARGE BLOCKS

1. PREPARATION OF SAMPLES

The samples were cut from single crystals of germanium grown in such a manner as to have reasonably uniform resistivity and long lifetime. The resistivity in each case was determined by making measurements on a bar cut from an adjacent part of the crystal. The body lifetime is estimated as follows. All of the surface of the sample is sand-blasted except for one small area. On this area a phosphor bronze point is set and formed. The sample surface is illuminated with a narrow slit of light a known distance away from the point; the rate of collection of minority carriers by the point is then determined as a function of the distance between the point and the line of the light. The body lifetime may then be estimated by standard theory¹⁴ assuming that the surface recombination velocity is large. The samples were about 1" square and $\frac{1}{2}$ " thick.

In order to make good ohmic contact to the sample, one face was plated with rhodium. The opposite face was then lapped or sand-blasted and given a two minute etch in CP4. The sides of the samples were covered with an insulating layer of Uclon lacquer.

2. APPARATUS

The apparatus used for the electrochemical measurements is shown in Fig. 1. The left-hand glass vessel contains the solution to be used. Into this is set the germanium sample, with the etched surface exposed to the electrolyte. The glass vessel also contains a loop of platinum wire for passing current. The germanium sample is held in position by setting it against a copper tube connected to a vacuum line: the copper tube also serves as a good electrical contact to the rhodium plating. The liquid in the germanium half-cell was stirred by means of a paddle. Electrical connection to the reference half-cell in the right-hand glass vessel is made through a salt-bridge. The reference half-cell used throughout the measurements consisted of silver-(silver oxide) in deci-normal potassium hydroxide solution. This half-cell has a potential of -0.41 volts against the standard hydrogen electrode where the symbol "—" means "more noble".

Arrangements were made, as shown in Fig. 1, to illuminate the germanium surface. Two sources of light were used. One, for steady illumination, consisted of an American Optical Company microscope illuminator. The intensity of the light from this source could be altered by

setting the iris diaphragm. For determining the surface photo effect on an ac basis, a second source, the light from which could be chopped at a convenient low frequency (about 40 cyc/sec), was used. The intensity of the chopped light could be controlled by choosing one of a series of fixed diaphragms.

The electrical circuit for the measurements is shown in Fig. 2. Dc measurements of electrode potential were made on a vacuum tube voltmeter. Measurements of the ac surface photo-voltage were made on a wave analyzer tuned to the fundamental of the chopper frequency. Each of these instruments had an input impedance of about 2 megohms, so that measurements were effectively made on open circuit. Anodic or cathodic current could be passed across the germanium half-cell by adjusting the setting of the current source, the internal impedance of which was also of the order of megohms. Arrangements were made so that the current could be switched in suddenly and switched out again after a short time. In order to avoid the accumulation of the product of electrochemical reaction at the germanium surface, measurements were taken by switching the current alternately in the anode and cathode direction. Such measurements were found to be sufficiently reproducible. Readings could be taken in a time of the order of half a second after switching on the bias current. In cases where there were changes with time, the values obtained immediately after switching on the current were adopted.

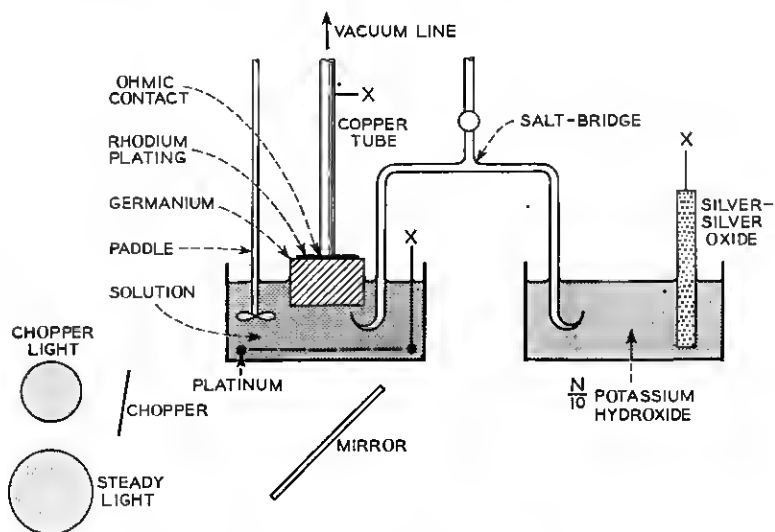


Fig. 1 — Experimental arrangement of apparatus.

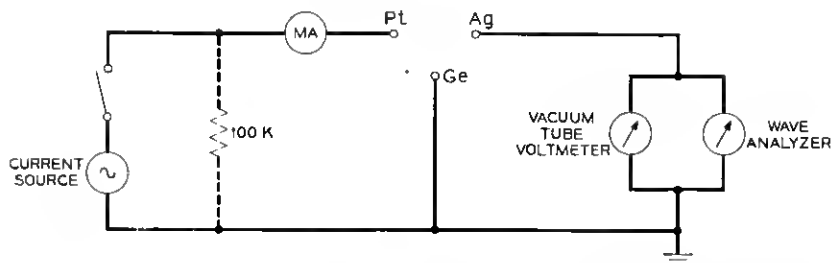


Fig. 2 — Electrical circuit for measurements of $(\partial V/\partial \alpha L)_I$ and V^E as functions of I^E and L .

3. PROCEDURE

3.1. Light Calibration

The relative light intensities corresponding to the different diaphragms in the light chopper were determined by measurements made with the thin slice technique (Section C). The absolute values of the light intensities may be estimated by taking these measurements and multiplying by the ratio of areas. There is some uncertainty involved in the latter process because, although attempts were made to insure that the intensity or illumination on the germanium surface was as uniform as possible, some non-uniformity remains. It may be assumed that the relative light intensities were known to about 5 per cent and the absolute magnitude to perhaps 25 per cent.

3.2. Measurements of Electrode Potential and Surface Photo Voltage

These could be started as soon as the freshly etched germanium sample was set into the electrolyte. It was however found that, during the first few minutes, there was a small but significant drift in these measurements. Sufficient time was therefore allowed to bring the surface into a steady-state condition. This process could be accelerated by switching a current of about 1 mA alternately in the anode and cathode sense several times.

Measurements were made as follows. The current desired could be set on the current source and switched into the germanium half-cell for a time sufficient to make the measurement of electrode potential and surface photo voltage. At each current, the chopper diaphragm was chosen in such a way that the surface photo voltage was about 5 millivolts, that is, small in comparison with kT/e , but large enough to be

measured accurately. Measurements were made in this way at a series of values of anode and cathode current.

The steady light was now switched on. The intensity of the steady light could be set equal to that produced by a standard chopper diaphragm in the following manner. The chopper was stopped and a standard diaphragm inserted. A suitable current was now passed through the electrolyte to bring the surface into a condition in which the measured electrode potential was extremely sensitive to light intensity. The iris diaphragm of the steady light was then adjusted until the steady light gave the same electrode potential as did the light from the standard chopper diaphragm. With the surface now maintained in this steady illumination, the set of measurements of electrode potential and ac surface photo voltage was repeated exactly as before. After completion of this set of measurements the iris diaphragm on the steady light was readjusted to such a setting that the new intensity of the steady light was equal to the sum of the previous steady light intensity and that given by the standard chopper diaphragm, i.e., twice that given by the standard chopper diaphragm. The measurements of electrode potential and surface photo-voltage as a function of anode and cathode current were then repeated. In this way a series of such measurements were made at light intensities equal to integral multiples of that given by the standard chopper diaphragm.

3.3. *To Verify Equation (5) Directly*

At each value of the electrolyte current, a series of readings of electrode potential and surface photo voltage was made, varying the setting of the steady light iris diaphragm. No attempt was made to estimate the intensity of the steady light at each point. The experiments were repeated at a series of anode currents for n-type material and at a series of cathode currents for p-type material.

3.4. *Direct Determination of the Over-Voltage Curve at Constant Minority Carrier Density*

As each value of electrolyte current, the steady light was adjusted to give some standard photo voltage. The electrode potential was then read and the process repeated at some other electrolyte current. Measurements made on n-type material in the anode direction in this way may then be compared with the p-type anode over voltage, and measurements made on p-type material in the cathode direction in this way with the n-type cathode over voltage.

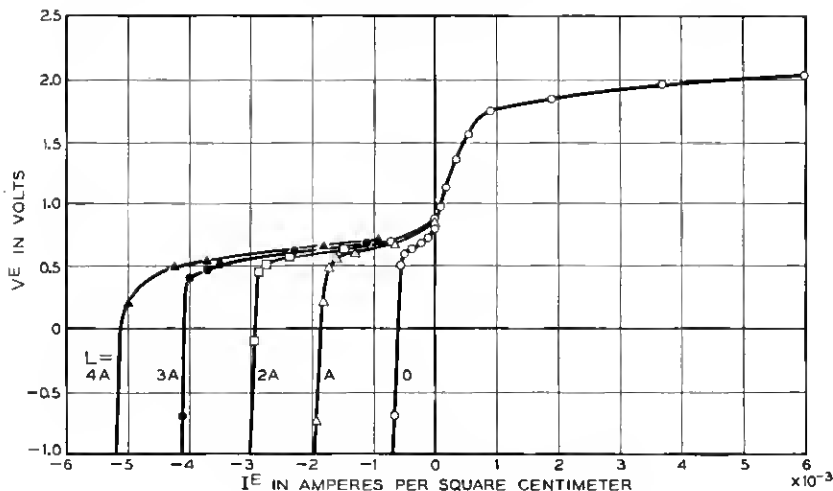


Fig. 3 — Plot of V^E against I^E for n-type in $N/10$ KOH, at different light intensities.

4. RESULTS

4.1. *n-Type in Decinormal Potassium Hydroxide*

$$\rho = 15 \text{ ohm cm.} \quad \tau > 4000 \text{ } \mu\text{sec.} \quad T = 27^\circ\text{C} \quad \text{area} = 5.4 \text{ cm}^2$$

Fig. 3 shows the observed relation between electrode potential and current in various steady lights. The lights used were multiples of the intensity A obtained with the $1\frac{1}{2}$ " diaphragm in the light chopper. It will be seen that in each case the current saturates very abruptly at some particular value in the anode direction. The saturation is not perfect, however. This is shown in Fig. 4, which shows measurements made in the dark extended to greater anode potentials. This graph shows that at sufficiently high anode potential extra current will pass even though the supply of minority carriers has been used up.

From Fig. 3 we may plot the anodic current flowing at some fixed potential, say $V^E = 0$, as a function of light intensity (Fig. 5). From equations (2) and (3) it follows that the slope of the curve should be αL . The value of αL for the standard light intensity is therefore found to be

$$\alpha A = 1.13 \times 10^{-3} \text{ amp/cm}^2$$

Postponing for the moment the question of the value of α , we now

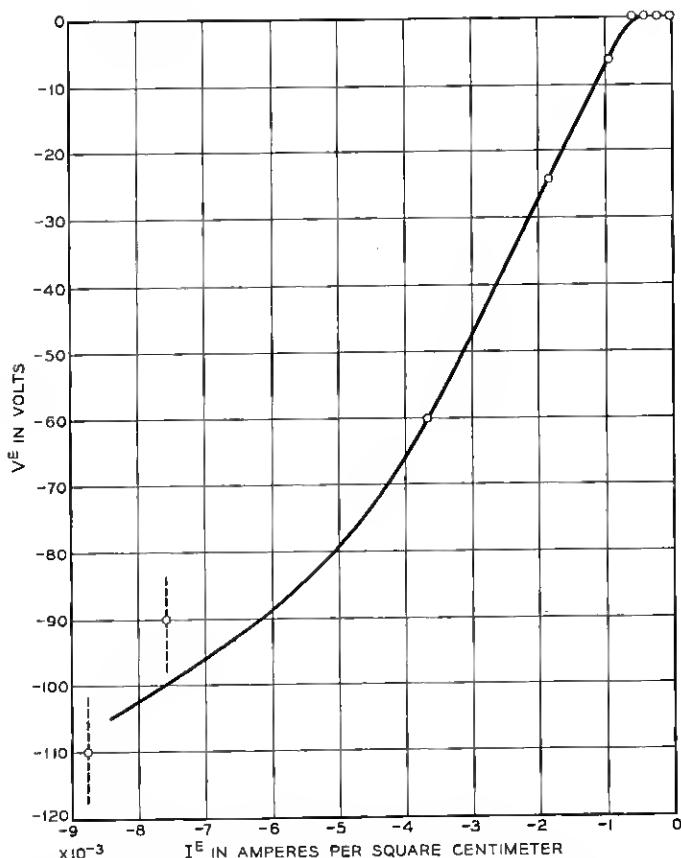


Fig. 4 — Plot of V^E against I^E for n-type, with no steady light, continued to large negative values of V^E .

know the value of αL for each diaphragm of the light chopper. From each reading of photo voltage therefore, it is possible to evaluate the quantity $(\partial V^E / \partial \alpha L)_{I^E}$. Fig. 6 shows this quantity plotted semi-logarithmically against electrode potential. The left-hand branch of the curve corresponds to a positive photo voltage; that is to say, the electrode potential increases on shining light on the surface. At the zero in photo voltage the sign of the photo voltage changes, the right-hand branch corresponding to a negative photo voltage. In zero light, the shoulder near $V^E = 0.8$ volts is rather indeterminate and depends on the exact condition of the surface. The dashed curve in Fig. 6 represents a second set of measurements taken on a subsequent day. This graph should be

compared with the curves showing surface photo effect as a function of contact potential, as found by Brattain and Bardeen in the germanium-gas experiments. The qualitative similarity is quite striking. The fact that the surface photo voltage in the left-hand branch eventually becomes very much larger than was found in the germanium-gas experiments is due to the depletion of holes caused by passing anode current across the germanium surface (Section A). If there were perfect saturation in the anode direction, one would expect that eventually the surface photo effect should become infinitely large. It will be seen that this is not so. The eventual limiting value, which is due to the second term in the right-hand side of equation (4), may be checked with the slope of Fig. 4.

The remainder of this section will be confined to a discussion of the surface photo voltage in the left-hand branch of the curve, where one is reasonably certain that equation (4) is satisfied. The cathode direction and the region of change in sign in surface photo voltage will be discussed in Section D. From equation (2), (3) and (4) one would predict that on plotting $\beta^{-1} (\partial \alpha L / \partial V^E)_{I^E}$ against I^E one should obtain straight lines of slope unity. This is shown in Fig. 7, in which the experimental points are compared with straight lines drawn with this slope.

Fig. 8 shows $[(\partial V^E / \partial \alpha L)_{I^E}]$ plotted logarithmically against V^E at a series of anode currents. From equation (5) the slope of these curves

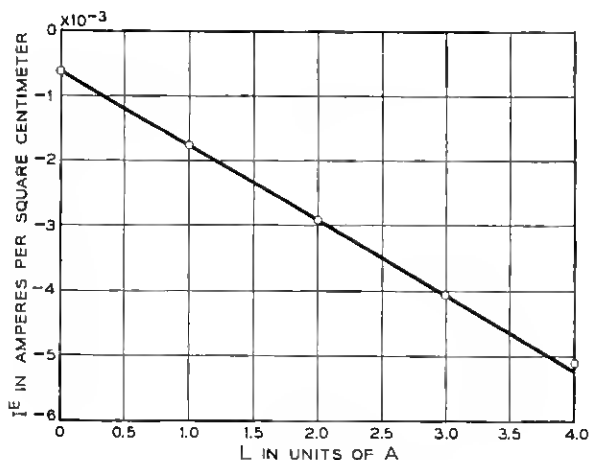


Fig. 5 — Plot of I^E at $V^E = 0$ for n-type as a function of light intensity in units of A.

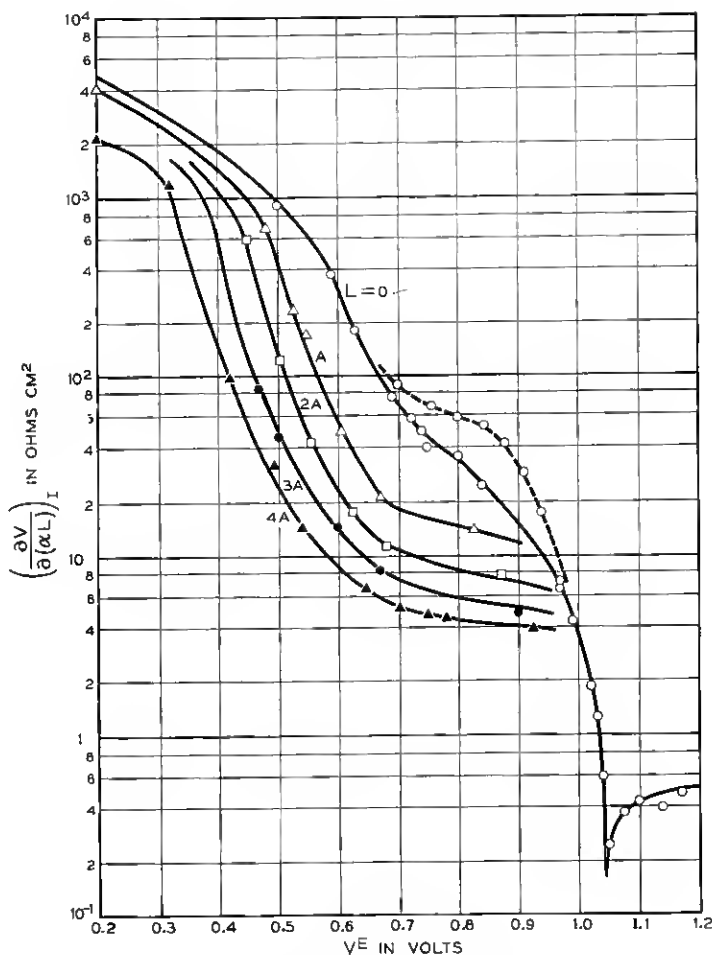


Fig. 6 — Plot of $(\partial V / \partial \alpha L)_I$ against electrode potential for n-type at various values of steady light.

should be β ; the lines drawn have a slope of 37 volts^{-1} , which is slightly less than the theoretical value of 39 volts^{-1} .

The horizontal displacement of the straight lines in Fig. 8, and the relation between V^E and I^E found for p-type material for anodic currents (see below), determine the Tafel over-voltage term in equation (1). Fig. 9 shows I^E plotted semilogarithmically against (i) V^E for p-type material; and (ii) the values of V^E at the intercepts in Fig. 8 of the con-

stant-current lines with the abscissa that gives the best fit with the p-type data, after allowing for IR drop in both cases. From equation (1), this abscissa must correspond with $(p_1/p) = 1$. Using this deduction, we may translate the vertical scale of Fig. 8 into a measure of (p_1/p) , see equation (4), as has been indicated on the right-hand side of that diagram. From the slope of Fig. 9, we have $K_A = 1.6$.

Now knowing the value of $(\partial \alpha L / \partial V^E)_I$ corresponding to $(p_1/p) = 1$, we may deduce from equation (4) the quantity αI_s , which is found to be 5.2×10^{-4} amps/cm². Another estimate is obtained from Fig. 7, from the intercept on the vertical axis corresponding to $I^E = L = 0$.

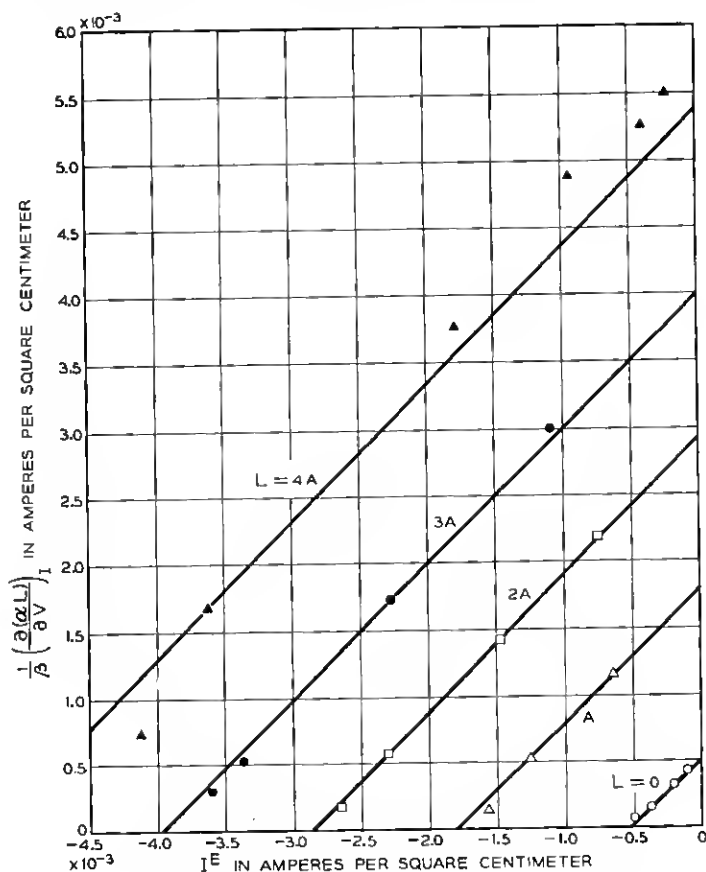


Fig. 7 — Plot of $\beta^{-1} (\partial \alpha L / \partial V)_I$ against I^E for n-type, at various values of light intensity.

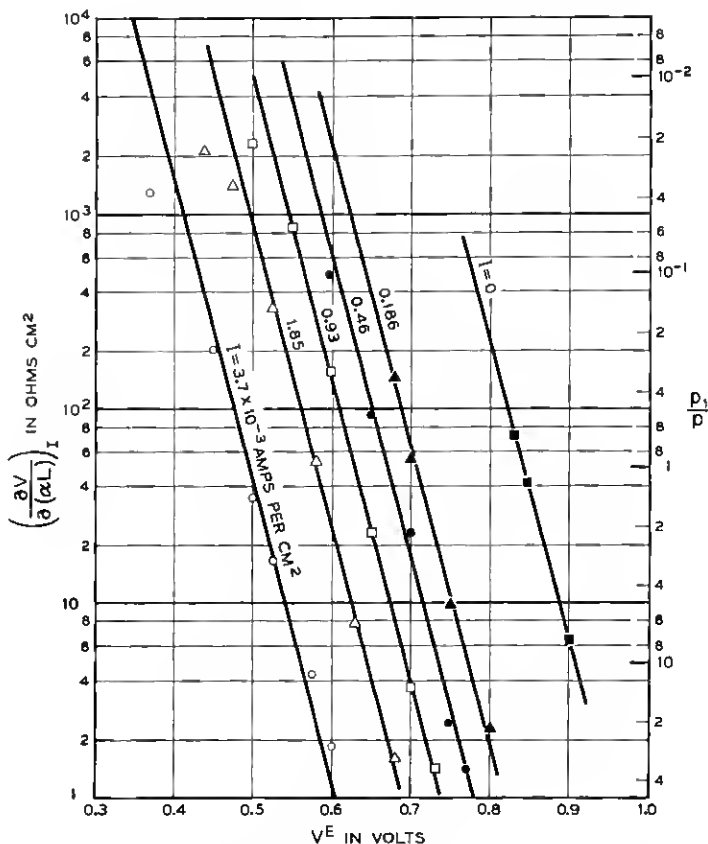


Fig. 8 — Plot of $(\partial V/\partial \alpha L)_I$ against electrode potential for n-type, at various values of anodic current. The scale on the right-hand side gives corresponding values of p_1/p .

This again gives $\alpha I_s = 5.2 \times 10^{-4}$ amps/cm². Both these estimates depend on the assumption that the second term in equation (4) is negligible: the evidence for this is that the curves in Fig. 8 are still substantially straight for some way above the abscissa corresponding to $(p_1/p) = 1$. A third estimate can be obtained by neglecting the leakage current Δ altogether, in which case αI_s is given by the intercept in Fig. 5 at $L = 0$. This gives 6.2×10^{-4} amps/cm². This value, as would be expected, is rather larger than the more accurate values obtained above.

In order to estimate α , one needs to know the magnitude of the standard light intensity. As mentioned earlier, this is difficult to do very ac-

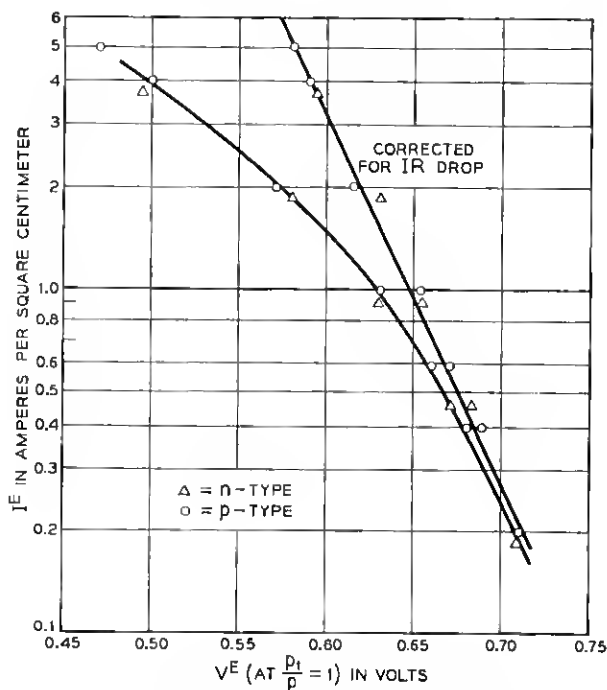


Fig. 9 — Anodic Tafel relation for both p and n type, allowing for ohmic drops in the circuit.

curately. A rough calibration, made using a photo-cell similar to the assembly used in the work of Section C, gave

$$A = 7.3 \times 10^{-4} \text{ amps/cm}^2$$

with this value of L , $\alpha = 1.6$. A better estimate of α for this material, obtained in the experiments described in the next section, is 1.80, in reasonable agreement with the above. Using $\alpha = 1.80$ and $\alpha I_s = 5.2 \times 10^{-4} \text{ amps/cm}^2$, we deduce

$$I_s = 2.9 \times 10^{-4} \text{ amps/cm}^2$$

Contributions to I_s come from thermal generation of minority carriers in the body, at the sides, and at the electrolyte surface itself. From the work in Appendix 1 it may be shown that, for a cylindrical block of radius r_0 that is thick in comparison with a diffusion length, the saturation current should be equal to $ep_0 V$, where

$$V = v_s + [D(1/\tau + 2v^*/r_0)]^{1/2}$$

where τ is the body lifetime, v^* is the surface recombination velocity at the sides of the cylinder, and v_s is that at the electrolyte surface itself. Using the experimental value of I_s and the value of p_0 deduced from the resistivity measurements, we find $V = 330$ cm/sec. In view of the facts that only a lower limit for τ is available, and v^* is not known at all, we can only make the crudest estimates of the various contributions to V . The experimental value would be obtained, for example, by setting $\tau = 4 \times 10^{-3}$ secs. and $v^* = v_s = 180$ cm/sec. The main conclusion to be drawn is that, even if V were entirely due to surface recombination at the electrolyte surface (which is certainly not the case), the surface recombination velocity at that surface would not be larger than that for a dry etched surface by a very considerable factor.

4.2. *p-Type Germanium in Decinormal Potassium Hydroxide*

$\rho = 7.5$ ohm cm $\tau > 1000$ μ secs. $T = 27^\circ\text{C}$ area = 5.6 cm²

The electrode potential V^E as a function of electrolyte current I^E and in various light intensities is shown in Fig. 10. (The light unit A was not quite the same as in the experiment on the n-type sample.) It will be noted that the saturation for p-type material in the cathode direction is less sharp than for n-type in the anode direction. In the cath-

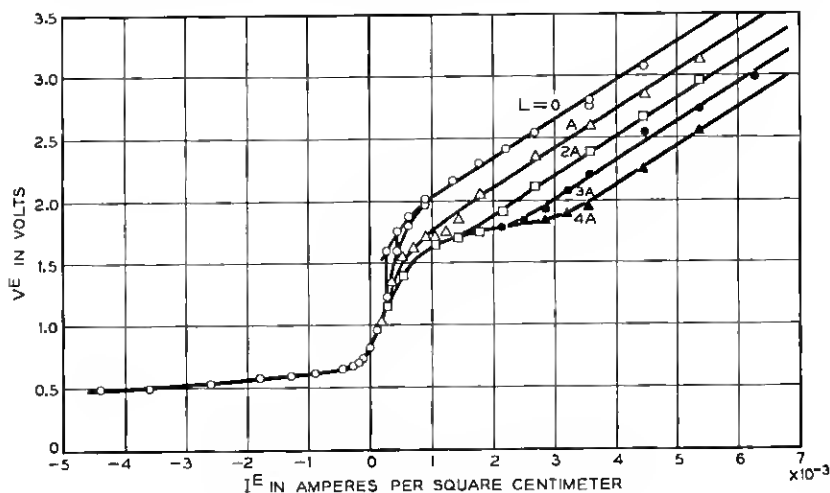


Fig. 10—Plot of V^E against I^E for p-type in $N/10$ KOH, at different light intensities.

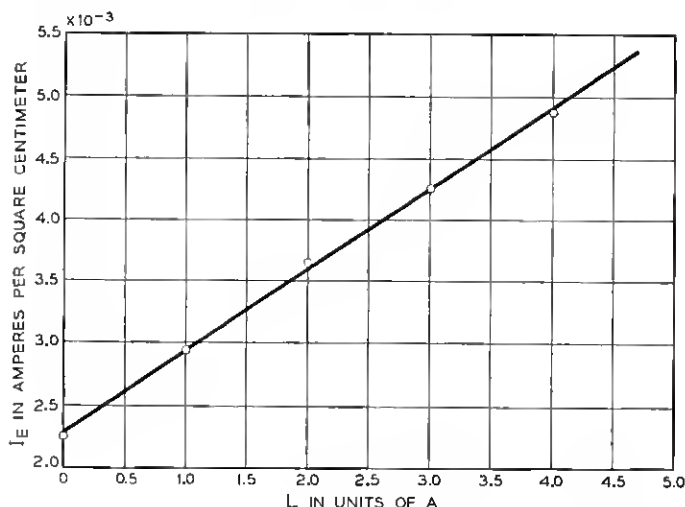


Fig. 11 — Plot of I^E at $V^E = 2.40$ volts for p-type as a function of light intensity in units of A.

ode direction there were two distinct regions of stable electrode potential: that for $V^E < 1.2$ volts, and that for $V^E > 1.8$ volts; for intermediate voltages, the readings were not steady, as might be expected if, in this region, there was a change-over from one electrode reaction to another. We have to consider the two regions separately. In Fig. 11, we have chosen $V^E = 2.4$ volts as a convenient value of voltage, and plotted I^E as a function of light intensity. From the slope, one deduces $\alpha L = 8.5 \times 10^{-4}$ amps/cm² for the unit of light intensity. A direct comparison of the α 's for the n and p-type samples, using the same intensity of illumination, gave $\alpha_A/\alpha_C = 1.93$. Thus, if $\alpha_A = 1.8$, $\alpha_C = 0.93$. Within the accuracy of the experiment, there is thus no current multiplication at a p-type cathode.

Fig. 12 shows $(\partial V^E/\partial \alpha L)_I^*$ as a function of V^E . It will be seen that this diagram is just the converse of Fig. 6: the smaller limiting value of the surface photo voltage is now in the anode direction, and the larger, which is lower than for the n-type sample because of the less perfect saturation, is in the cathode direction. (The limiting value may again be checked with the slopes of the saturation lines in Fig. 10.) In Fig. 13, the quantity $\beta^{-1}(\partial \alpha L/\partial V^E)_I$ is plotted against I^E . The straight lines are in the predicted positions, using the theoretical value of β .

* For the balance of this section, the symbol α means α_C .

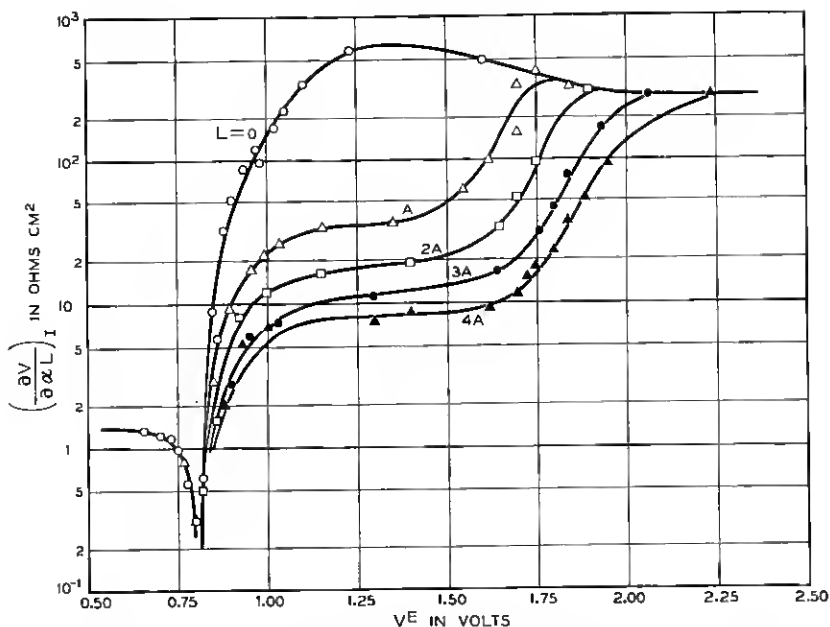


Fig. 12 — Plot of $(\partial V/\partial \alpha L)_I$ against electrode potential for p-type near the change in sign of the photo-effect, at various values of steady light.

Fig. 14 is the analogue of Fig. 8: $(\partial V^E/\partial \alpha L)_I$ is plotted logarithmically against V^E for a selection of cathode currents. The lines are drawn with their theoretical slopes. Agreement is again adequate, although not so good as in Fig. 8. The poorer saturation is again obvious in this figure, in that the experimental curves quickly depart from linearity in the section of the figure corresponding to exhaustion of electrons.

Fig. 15 has been constructed in the same way as Fig. 9, and contains points both for p-type and for n-type germanium. From the slope, the Tafel coefficient K_c in this region appears to be 4.3, which seems rather large. Notice that the Tafel coefficient for the lower cathode region may be quite different. (See Section D.) In constructing Fig. 15, we are able to deduce, in the same way as for n-type material, the value of $(\partial V/\partial \alpha L)_I$ corresponding to $(n_1/n) = 1$, although in this case the result is much less reliable. The resulting translation of the vertical scale of Fig. 15 into (n_1/n) is shown on the right-hand side of that figure. The corresponding value of αI_s is about 5×10^{-4} amps/cm². It is difficult to check this, as we did for the n-type measurements. If the values of $(\partial \alpha L/\partial V^E)_I$ taken in zero steady light are plotted against I^E (see Fig. 13), the resulting

curve does not even approximate to a straight line: at lower currents, the situation is complicated by the changeover to the anode reaction (see Section D), and at higher currents, by the imperfect saturation and instability of V^E . If, nevertheless, we extrapolate this curve to zero current by using the theoretical slope, we get $\alpha I_s = 2.7 \times 10^{-4}$ amps/cm². Under the circumstances, this does not agree too badly with the value obtained by comparing the n-type and p-type Tafel curves. We conclude that the electron saturation current for the p-type sample is of the same order of magnitude as the hole saturation current for the n-type sample. This means that the surface recombination velocities are not too different. We discuss the ratio of surface recombination velocities in the two current directions in Section D. Notice, however, that the quantity I_s is in any case significant only when (n_1/n) is neither 0 nor 1; for the case of almost complete electron exhaustion, corresponding to the higher points in Fig. 10, it is immaterial whether we ascribe the extra current flowing to the leakage current Δ or to increasing I_s . On the grounds of convenience we prefer the former description.

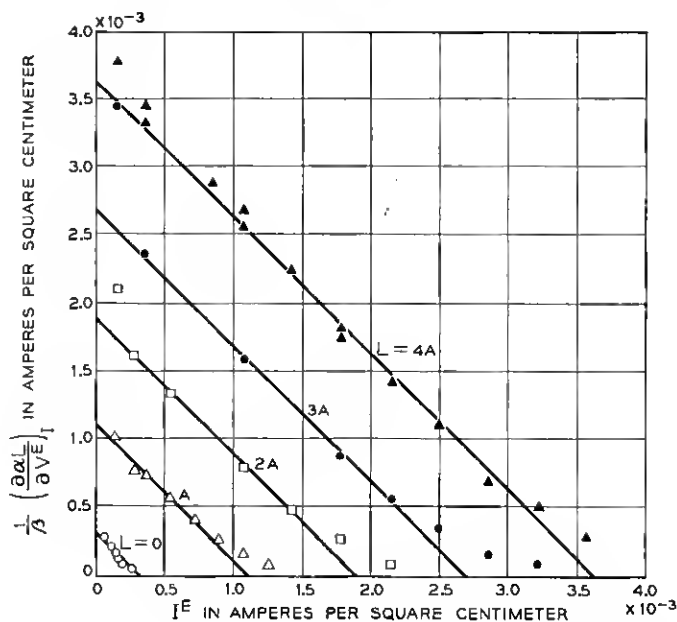


Fig. 13 — Plot of $\beta^{-1} (\partial \alpha L / \partial V^E)_I$ against I^E for p-type at various values of light intensity.

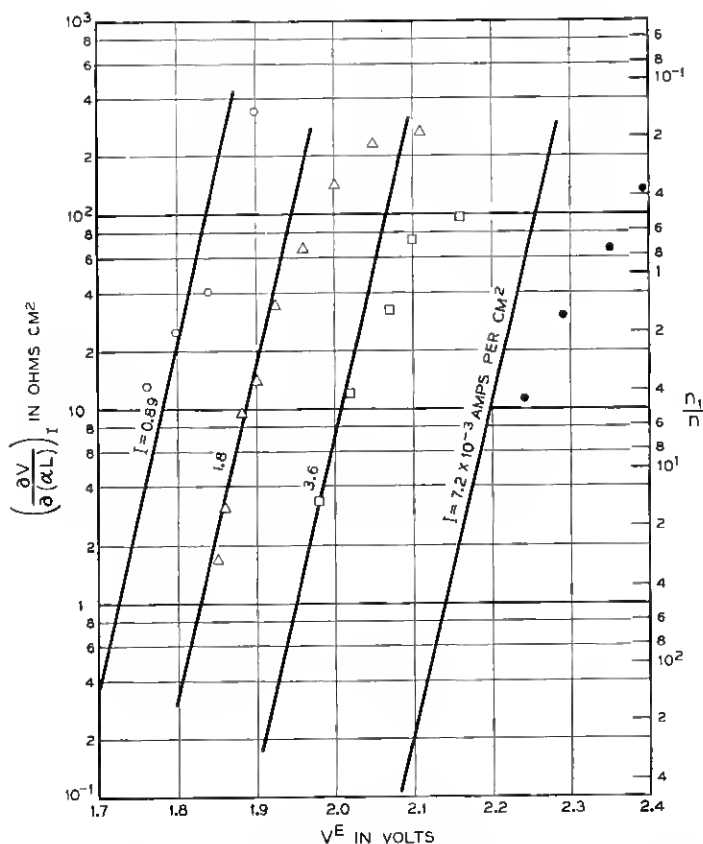


Fig. 14 — Plot of $(\partial V / \partial \alpha L)_I$ against electrode potential for p-type, at various values of cathodic current. The scale on the RHS gives corresponding values of n_1/n .

4.3. Experiments in Other Electrolytes

Experiments have also been carried out in solutions of potassium chloride and hydrochloric acid. Fig. 16 shows the relation between electrode potential and current in these three electrolytes, the effects of depletion of electrons or holes having been removed from the curves. Notice that the potassium chloride solution behaves like hydrochloric acid in the anode direction and like potassium hydroxide in the cathode direction. This may be because in the case of potassium chloride, the pH of the solution in the vicinity of the electrode is extremely dependent on the progress of the electrode reactions. The extreme difference be-

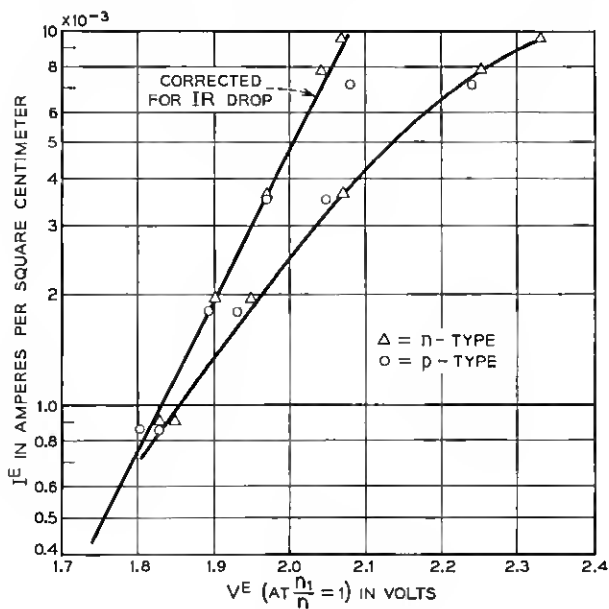


Fig. 15 — Cathodic Tafel relation for both p and n type, allowing for ohmic drops in the circuit.

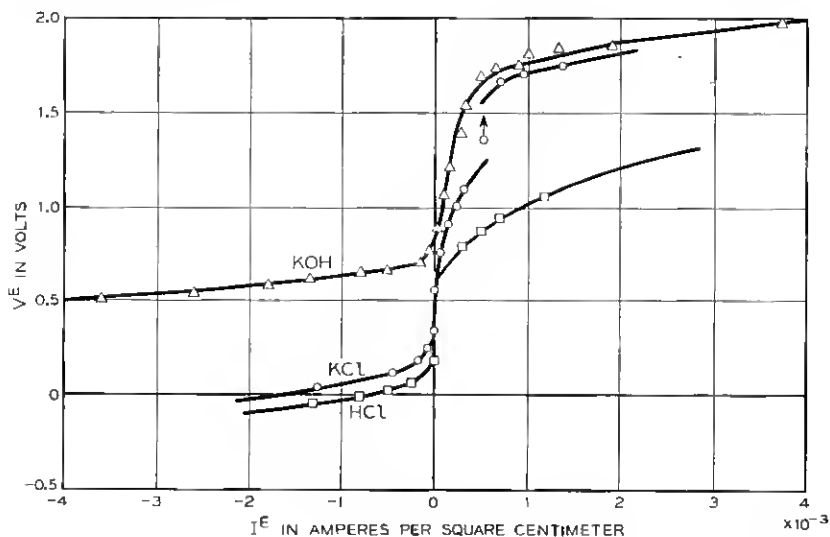


Fig. 16 — Plot of V^E , for equilibrium minority carrier density, as a function of I^E , in various electrolytes.

tween the potassium hydroxide and hydrochloric acid curves, which are roughly parallel, is about 700 millivolts, which is roughly equal to the change in the hydrogen electrode potential in going from pH1 to pH13. Differences between the three solutions were, however, observed. Specifically it was found that, whereas in potassium hydroxide cathode potentials higher than 1.80 volts were stable, no such stability was found in hydrochloric acid. Potassium chloride represented an intermediate case, behaving for the first minute or so like potassium hydroxide and then abruptly changing over to the hydrochloric acid behavior. For both hydrochloric acid and potassium chloride with p-type material it was found that, at the same time as the electrode potential was changing, the initially large photo-voltage decreased with time, went through zero, and was replaced by a small photo-voltage of the opposite sign. This one must understand as follows. The primary cathode reaction, occurring in the first few seconds, is with electrons, and, because the electrode reaction tends to deplete electrons from the p-type material, a large barrier can be built up. After this reaction has proceeded for some time, its place is taken by another reaction involving holes which are plentiful in the p-type material. This results in a change in the observed electrode potential and a change in sign of the photo voltage.

C. THIN SLICES

1. EXPERIMENTS ON THIN SLICES

As mentioned earlier, it is possible, by making measurements on a thin slice of n-type germanium with a rectifying junction on the far side, to follow changes in hole density as these occur. The hole density near this rectifying junction is in fact determined by measuring the floating potential V_f . Measurements of this type enable one to demonstrate directly that equation (1) is true for anode currents irrespective of the validity of equation (2) and (3). Experiments with this geometry also enable one to determine the current multiplication factor α directly. Extra holes in the n-type region may be created in two ways: by shining light on the sample or by passing current across the rectifying junction in the forward direction. One may therefore calibrate the light intensity directly, by comparing the changes in the electrode properties produced by a given light with the changes produced by passing a given current across the rectifying junction.

The further analysis of these experiments however is complicated. The geometry is much less nearly one-dimensional, because of recomb-

nation at the sides, in the body and at one or both surfaces. Not all of the minority carriers injected from one side will reach the other. Also, the series resistance in this geometry is necessarily much larger than with a large block. In any case, the analysis duplicates to a large extent the experiments described in Section B. We therefore confine ourselves to describing such experiments as cannot be done with the large block technique.

2. MATERIAL AND GEOMETRY

The samples used consisted of M-1777 p-n-p power transistors, without collectors. The base material consisted of slices of germanium 4 mils thick and $\frac{1}{4}$ inch square. The ohmic contact consisted of a circle of gold wire bonded into the germanium. Within this circle and on the same side of the germanium a regrown rectifying junction 120 mils in diameter, made by the indium alloying technique, was attached. Two germanium samples were used for the fabrication of these units, having resistivities of 4 ohm cm and 15 ohm cm, the latter being from a slice cut close to the n-type sample used in the experiments of Section B. Contacts were arranged to the gold and to the indium.

The opposite face of the germanium was masked with a piece of bakelite $\frac{1}{32}$ " thick, having a hole in the middle equal in size to the indium rectifying junction (Fig. 17). The bakelite was attached to the germanium surface with Ucilon lacquer. Care was taken to protect the edges of the unit with the same lacquer in order to insulate exposed parts of the gold spiral from contact with the electrolyte. The unit was set into the electrolyte as in Fig. 1, care being taken to see that no bubbles were left in the region of the exposed germanium surface. The tip of the salt bridge was set directly under the exposed region. With this geometry one had to be especially careful to see that current was not left on for too long in either direction in order to minimize the accumulation of

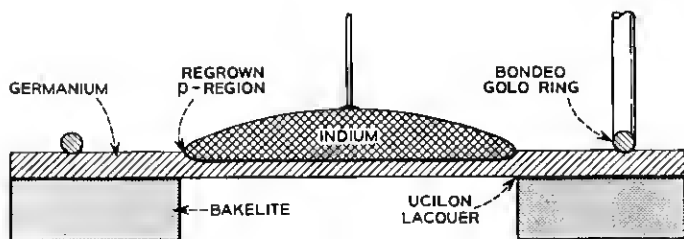


Fig. 17 — Diagram of thin-slice unit assembly.

gases or other reaction products in the confined space around the germanium.

3. PROCEDURE

3.1. *Light Calibration*

For calibration of the chopped light one can conveniently measure currents collected at the rectifying junction on a short-circuit basis (Fig. 18). For this purpose the unit may either be set into the electrolyte or left directly above it: in the latter case, however, the corrections for the change in reflection coefficient and for the removal of one reflecting surface are a little uncertain. For calibration of the settings of steady light which are used in the experiment, it is convenient to take a series of measurements of V^R , the voltage between the alloy junction and the base, as a function of I^R , the current flowing between the alloy junction and the base. By fitting the experimental points, with and without the steady light, on to the same rectifier curve, one may deduce the value of the photo current collected by the rectifying junction.

3.2. *Relation between floating potential and electrode potential, and determination of α by illumination*

The steady light is fixed at some value, determined as above. Measurements are made of electrode potential V^E and of the voltage V^R between the alloyed junction and the base, as functions of the electrolyte current. This is then repeated at other values of the steady light.

3.3. *Determination of α by current injection*

The above procedure is repeated, without steady light, at a series of values of current I^R across the alloyed rectifying junction.

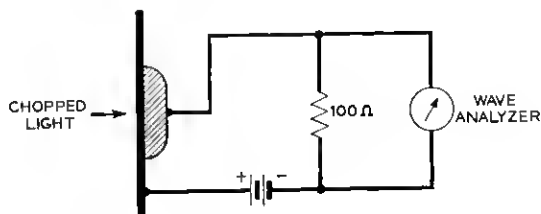


Fig. 18 — Electrical circuit for light calibration with thin-slice unit.

4. ANALYSIS OF THE EXPERIMENTS — RESULTS

In writing equation (2), we considered only minority carriers created at or very near the surface across which the electrolyte current is passing. We now wish to modify this equation to include minority carriers injected from the far surface, that is, across the rectifying junction. Since the floating potential at this junction measures the minority carrier density there rather than at the electrolyte surface, we should like also to be able to relate these two quantities. It may be shown (see Appendix 1) that the effect of recombination at the sides, in the body and at both surfaces may be described by writing

$$\left(\frac{p_1}{p}\right)^E = 1 + \frac{I_p^E + L + \gamma' I_p^R}{I_s} \quad (8)$$

$$\left(\frac{p_1}{p}\right)^R = 1 + \frac{\gamma''(I_p^E + L) + I_p^R}{I_s} \quad (9)$$

where γ' and γ'' are quantities slightly less than 1, analogous to the forward and reverse α 's of a junction transistor. Since the slice of germanium is thin in comparison with a body diffusion length, and since the surface recombination velocities at the rectifying junction and at the electrolyte junction are fairly low, it will be sufficient to suppose that most of the generation and recombination takes place by diffusion to the sides. Under these conditions it is a sufficient approximation to write $\gamma' = \gamma'' = \gamma$. It is sufficient to suppose that

$$I_p^R = I^R$$

because it is known that almost all of the current crossing an indium regrown junction on n-type germanium is hole current, that is, the emitter efficiency is very close to 1.

We are now in a position to analyze experiments described in the preceding paragraph.

(a) Set $I_p^E = 0$. Then, since

$$\left(\frac{p_1}{p}\right)^R = e^{\beta V_f}$$

and

$$V^A = V_f + I^R R_{spr.}$$

we have, from equation (9)

$$V^R = I^R R_{spr.} + \frac{1}{\beta} \ln \left[1 + \frac{\gamma L + I^R}{I_s} \right] \quad (10)$$

Thus by taking a series of measurements of I^R and V^R we may determine the quantity γL for each light intensity.

(b) The difference between $(p_1/p)^E$ and $(p_1/p)^R$ will be relatively unimportant unless one of them is close to zero. Now, if the electrolyte current is near its saturation value, $(p_1/p)^E$ is effectively zero. But, however low the hole density at the lower surface may be, the hole density close to the rectifying junction can not be lower than is allowed by local hole generation. The lowest value of $(p_1/p)^R$ is determined by equations (8) and (9) to be

$$\left(\frac{p_1}{p}\right)^R = e^{\beta V_{f^{\min}}} = 1 - \gamma \quad (11)$$

Using equation (11) we may correct for the above effect and determine $(p_1/p)^E$ from V_f at all values of electrolyte current:

$$\left(\frac{p_1}{p}\right)^E = \frac{e^{\beta V_f} - e^{\beta V_{f^{\min}}}}{1 + e^{\beta V_{f^{\min}}}} \quad (12)$$

Using this equation one may take the experimental results and use them

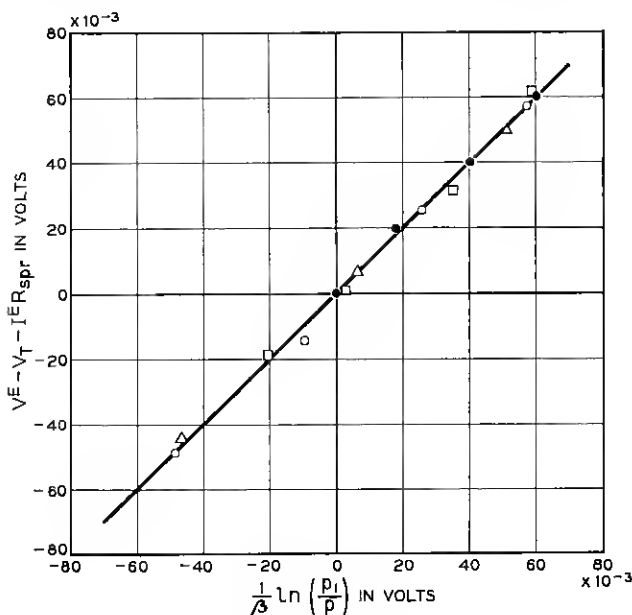


Fig. 19 — Plot of the quantity $(V^E - V_T - I^E R_{spr.})$ against $\beta^{-1} \ln (p_1/p)$.

to provide a direct verification of equation (1). This is shown for the 15 ohm cm sample in Fig. 19 in which we have chosen the Tafel over voltage parameter K_A in such a way that, by plotting the quantity against

$$\beta^{-1} \ln (p_1/p)^{\frac{1}{2}}$$

against

$$[V^E - V_{\text{Tafel}} - I^E R_{\text{spr}}.]$$

the curves corresponding to different currents are superimposed on one another. It will be seen that the result is a straight line of slope unity. This may be regarded as the most direct experimental evidence for equation (1) available at the present time. The value of K_A used in the construction of this graph was 2.2 which is in reasonable agreement with that determined in Section B.

Two further observations are relevant. With the sample in the dark and no electrolyte current flowing, it was not possible to detect any significant departure of the floating potential from zero. This enables one to put an upper limit on the hole current which is flowing when the applied external current is zero as a result of some corrosive process. Since the smallest floating potential which could have been detected is of the order of 1 millivolt, one concludes that the maximum net hole current which could be flowing is $10^{-3} \beta I_s$, which is about $2 \mu\text{A}/\text{cm}^2$. The other observation concerns the dependence of floating potential upon cathode current. After making due allowance for the potential

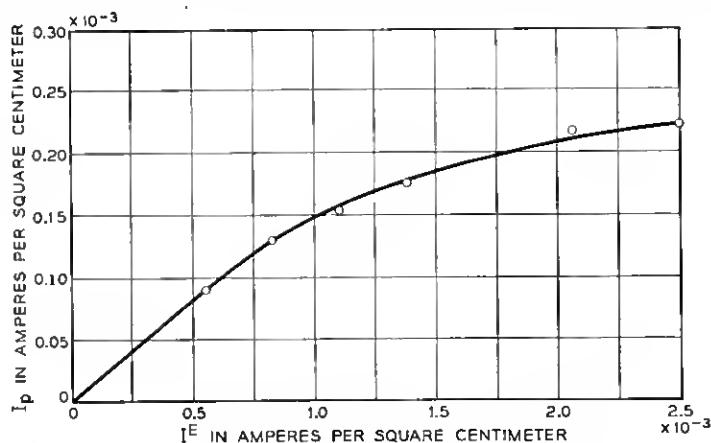


Fig. 20 — Injection of minority carriers on n-type germanium for cathodic currents.

drop across the spreading resistance, one may deduce the rate of injection of holes as a result of the cathodic reaction at the surface. This is shown in Fig. 20, in which the hole current as deduced from the measurements and from equation (2) is plotted directly against cathode current. It will be seen that the amount of injection is quite small. This is in agreement with the general observation that the principal reaction in the cathode direction is with electrons.

(c) From the measurements in various lights one may plot a curve showing the limiting electrolyte current, at some suitable value of V^E , as a function of the quantity γL deduced from the light calibration. Assuming as usual that the quantity Δ (see equation 2) is a constant at a constant electrode potential, one should have

$$I^E = -\frac{\alpha}{\gamma}(\gamma L) + \Delta - \alpha I_s \quad (13)$$

Fig. 21 shows this curve plotted for a 4-ohm cm sample. From the slope of this graph one has $\alpha/\gamma = 1.77$. A similar plot for the 15-ohm cm sample gave $\alpha/\gamma = 1.90$. The values of γ as deduced from the minimum floating potential (see above) were 0.83 and 0.95 respectively, thus giving $\alpha = 1.48$ on the 4 ohm cm sample and 1.80 on the 15 ohm cm sample. The reason for this apparent dependence of α on resistivity is not known.

If in the same way we take the current-injection data, and plot I^E against I^R at some fixed value of V^E , we should have:

$$I^E = -\alpha\gamma(I^R) + \Delta - \alpha I_s \quad (14)$$

This plot is also shown in Fig. 21 for the 4-ohm cm sample. The slope

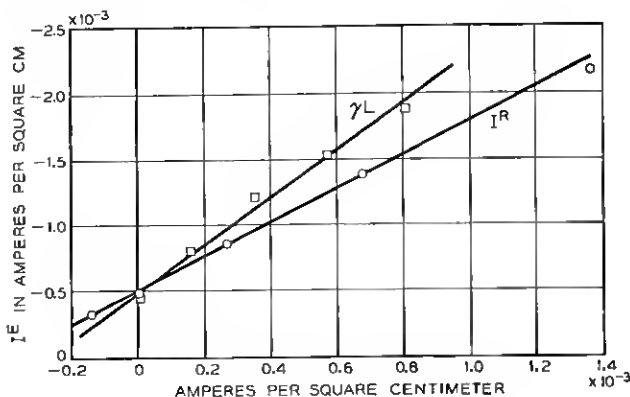


Fig. 21 — Plot of I^E as a function of γL or I^R .

of this curve should be $\alpha\gamma$. The experimental value is 1.30; this gives $\alpha = 1.56$, which checks well enough with the value obtained by illumination of the surface. It is also possible to deduce the quantity I_s for the thin slice geometry. However, as has been explained, the interpretation of this quantity is complicated by recombination at the edges of the sample and the flow is far from one-dimensional. In addition, the saturation in the thin slice experiment is usually poorer than that found on the large blocks. The reason for this is not known. It is possible that the sharpness of saturation may depend on the exact state of the surface; it is more difficult to prepare the thin slice samples in such a way that the surface is in a clean and reproducible condition. It is just possible that poorer saturation found with the thin-slice samples could be ascribed to leakage across the insulating lacquers.

D. THE REGION OF CHANGE IN SIGN OF THE PHOTO VOLTAGE

In the preceding sections we have discussed the experimental results obtained for anodic currents with n-type material, and for cathodic currents with p-type material. Throughout these regions, the surface photo-voltage would have the constant value $1/\beta I_s$ if it were not for enhancement or reduction of the density of minority carriers near the surface. (Equation (4) and its analogue for p-type material.) Looking at Figs. 6 and 12, we may say that, if the experimental values found in the upper parts of the higher branch for each sample were corrected by multiplying by the appropriate ratio of minority carrier concentrations (and of course for imperfect saturation), the corrected photo-voltage would be constant throughout the regions mentioned, and would be approximately equal to those corresponding to the shoulders seen in the "dark" curve in Fig. 6 and in Fig. 12. Figs. 6 and 12 would then look very much like the curves of surface photo-voltage against contact potential given for the germanium-gas case by Brattain and Bardeen. We now turn our attention to the remaining sections of Figs. 6 and 12, in which the surface photo-voltage, quite irrespective of variations in minority carrier density, is changing with electrode potential.

We consider the ratio of the limiting anode and cathode values first, taking equations (1) and (6) as the basis for our discussion. Equation (1) says that the magnitude of anodic current flowing under given conditions is a function of the difference between V^E and the imref φ_{ps} for holes just inside the space-charge region, since φ_{ps} is related to the hole concentration at this point by the equation

$$\varphi_{ps} = \varphi_0 + \beta^{-1} \ln (p_1/p). \quad (15)$$

(φ_0 is the equilibrium hole imref.) If then the electrolyte current is held constant, and the hole imref changed (for example by shining light onto the sample), the change in electrode potential must be equal to the change in hole imref — a quantity which has the same sign for p as for n type, but a much smaller magnitude. On this basis we may derive the surface photo-voltage for both n and p type under conditions of anodic current (see Appendix 2):

$$\left(\frac{\partial V^E}{\partial L}\right)_I = \frac{1}{\beta I_{ps}^A} \text{ (n-type)} \quad \left(\frac{\partial V^E}{\partial L}\right)_I = \frac{nb}{p} \frac{1}{\beta I_{ns}^A} \text{ (p-type)} \quad (16)$$

for $p_1/p = 1$ (b = ratio of electron to hole mobility.) Here the suffixes n and p distinguish electron and hole saturation currents, and A specifies the recombination current, and therefore the surface recombination velocity, corresponding to anodic conditions.

Similarly, equation (6) says that the magnitude of cathodic current is a function of the difference between V^E and the imref φ_{ns} for electrons just inside the space-charge region. From an argument identical with that given above, we deduce the following values for the surface photo-voltage under cathodic conditions:

$$\left(\frac{\partial V^E}{\partial L}\right)_I = -\frac{p}{nb} \frac{1}{\beta I_{ps}^C} \text{ (n-type)} \quad \left(\frac{\partial V^E}{\partial L}\right)_I = -\frac{1}{\beta I_{ns}^C} \text{ (p-type)} \quad (17)$$

for $n_1/n = 1$.

Using these relations, we may compare the minority carrier saturation currents in the anode and cathode directions for the two samples:

$$\begin{aligned} \frac{I_{ns}^C}{I_{ns}^A} &= -\frac{(\partial V^E/\partial L)_{\text{an}}}{(\partial V^E/\partial L)_{\text{cath}}} \bigg/ \left(\frac{nb}{p}\right) = \frac{100}{40} = 2.5 \\ \frac{I_{ps}^C}{I_{ps}^A} &= -\frac{(\partial V^E/\partial L)_{\text{cath}}}{(\partial V^E/\partial L)_{\text{an}}} \bigg/ \left(\frac{p}{nb}\right) = \frac{180}{100} = 1.8 \end{aligned} \quad (18)$$

Within the accuracy of the experiment, we conclude that the ratio is about 2 in each case. Since surface recombination velocity at the electrolyte surface accounts for only part of the total minority carrier recombination current, the ratio of the surface recombination velocities in the cathode and anode conditions must be somewhat larger than this. For the balance of this section, however, we shall ignore the difference between the anodic and cathodic values of I_* .

In the intermediate region, the simplest interpretation is that the electrode reaction is neither wholly anodic nor wholly cathodic, irrespective of whether the *net* electrolyte current is anodic or cathodic. We sup-

pose that the anodic and cathodic processes are still described by equation (1) and (6), but that the net current is now the sum of the currents appearing in those two equations. Dropping the IR terms from equations (1) and (6), and rewriting in terms of currents instead of voltages, we have:

$$\begin{aligned} I_A^E &= I_{0A}[\exp[-(\beta/K_A)\{V^E - V_{0A} - (\varphi_{ps} - \varphi_0)\}] - 1] \\ I_C^E &= I_{0C}[\exp[+(\beta/K_C)\{V^E - V_{0C} - (\varphi_{ns} - \varphi_0)\}] - 1] \\ I^E &= I_C^E - I_A^E \end{aligned} \quad (19)$$

With $\varphi_{ps} = \varphi_{ns} = \varphi_0$, equations (19) have the form of two imperfect rectifiers in shunt, arranged in the opposite sense one to another; a large voltage applied in either direction will cause a large current to flow through one, while only the comparatively small "saturation current" (I_{0A} or I_{0C}) flows through the other. (This is why we are able to ignore cathodic processes when there is a large current in the anodic sense and vice versa.) Using the method given in Appendix 2, we may show for n-type semiconductor in the limit $p_1/p = 1$ and $n_1/n = 1$, which is certainly appropriate to the measurements made at small currents and with no steady light,

$$\left(\frac{\partial V^E}{\partial L}\right)_{I^E} = \frac{1}{\beta I_s} \frac{1 - (X/X_0)}{1 + (nb/p)(X/X_0)} \quad (20)$$

where

$$X = \exp\left[\beta\left(\frac{1}{K_A} + \frac{1}{K_C}\right)V^E\right], \quad \text{and}$$

X_0 , which is the value of X for which the surface photo-effect vanishes, is given by:

$$X_0 = \frac{bn}{p} \frac{I_{0A}}{I_{0C}} e^{\beta((V_{0A}/K_A) + (V_{0C}/K_C))} \quad (21)$$

The expressions for p-type are analogous.

This may be tested by plotting the quantity

$$Q = \ln\left\{\left[1 - \frac{(\partial V/\partial L)}{(\partial V/\partial L)_{\text{cath}}}\right] \bigg/ \left[1 - \frac{(\partial V/\partial L)}{(\partial V/\partial L)_{\text{an}}}\right]\right\}$$

against V^E (Fig. 22). This gives a straight line for both samples; from the slope one deduces $1/K_A + 1/K_C = 1.0$. The value of K_A deduced from the measurements at larger anodic currents was about 2; this suggests that K_C is about 2 also. (Note that this is not necessarily the same

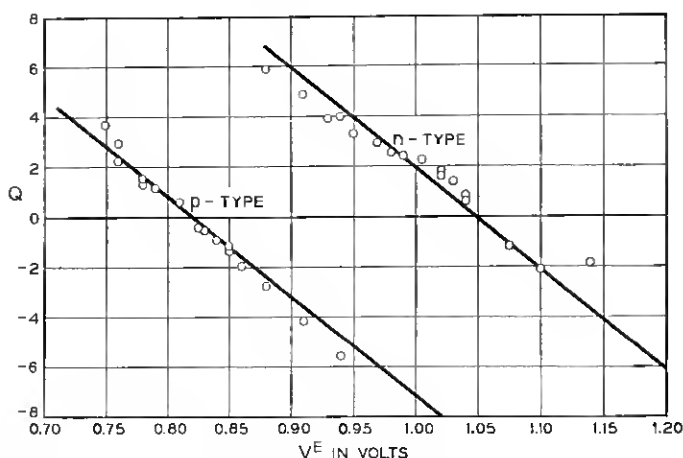


Fig. 22 — Plot of the quantity Q against electrode potential for p and n type germanium.

cathodic process as that represented by the Tafel curve in Fig. 15, since this is below, the other above, the region of voltage instability.)

Equation (21), and its analogue for p-type material, depends on resistivity only through the factor (bn/p) . To test this, we make use of the difference between the values of V^E at which the surface photo-voltage vanishes for the n and for the p-type sample. Using the value of $(1/K_A + 1/K_C)$ deduced above, we may construct the following table:

Sample	n-type	p-type
V^E for $I^E = 0$	0.83 volts	0.84 volts
V^E for which $(\partial V/\partial L) = 0$	1.05	0.82
$\frac{K_A K_C}{K_A + K_C} \frac{1}{\beta} \ln \frac{(\partial V/\partial L)_{\text{catb}}}{(\partial V/\partial L)_{\text{anb}}}$	-0.12	0.12
Sum of second and third lines	0.93	0.94

The voltages in the last line of the table are, within the experimental error, the same for the two samples, thereby checking (as one would expect) that the purely electrochemical features of the electrode processes near zero current, as opposed to those which depend on the hole or electron concentrations, are independent of the type of germanium used.

It is not possible to deduce the separate values of the quantities V_{0A} , V_{0C} , I_{0A} , and I_{0C} . In principle, the equilibrium potentials could be

deduced from thermodynamical reasoning from heats of reaction, but we are ignorant as to the exact nature of the reactions taking place. We can however draw one rather interesting conclusion from the fact that the zero in photo-voltage for a sample having $nb/p = 1$ occurs at a potential about 0.1 volts higher than that corresponding to zero current. This one may understand as follows. When the net current through the surface is zero, the anodic and cathodic currents I_A^E and I_C^E are equal in magnitude and opposite in sign. (We know from the work of Section C that each is of the order of $1\mu A/cm^2$ or smaller.) Since in this state the surface is on the anodic or p side of the zero in photo voltage, it follows that, if a small current is allowed to cross the surface, almost all of it will be represented by change in I_A^E and very little by a change in I_C^E . We may in fact show from equations (19) and (21) that, if δV represents the difference between electrode potential corresponding to zero current, and that at which the photo-voltage vanishes for a sample having $p/nb = 1$, then the ratio of cathodic (electron) to anodic (hole) current for a small displacement from the zero-current condition is given by:

$$\frac{K_C}{K_A} e^{\beta((1/K_A)+(1/K_C))(\delta V)} \quad (22)$$

From the experimental values, this ratio is about 0.03. This, of course, is true whether the net current into the germanium from the solution is positive or negative. If we may identify the anodic process with oxidation of germanium, this result shows that, at sufficiently small currents, the predominant process is either oxidation of germanium or reduction of germanium oxide, depending on the sign of the external current, and that it is only at higher cathodic currents that some other process, represented by I_C^E , takes over. Whether or not the alternative process is plating out of hydrogen (which should take place somewhere near this voltage) we do not know.

It should be mentioned here that the voltage difference δV does not vary much with electrolyte, although the separate voltages may change considerably. One reason for this may be that V_{0A} and V_{0C} are shifted by equal amounts when the pH of the solution is changed. One may tentatively conclude that the surface of a sample of germanium in contact with an aqueous electrolyte, with no net current crossing the surface, is p-type in character whether the measured electrode potential is high or low.

E. CONCLUDING REMARKS

(1) The primary reaction at a germanium anode is with holes rather than with electrons in the semiconductor. The evidence for this is that

the measured electrode potential in the anode direction depends on the concentration of holes near the surface in the way to be expected from the purely thermodynamical reasoning given in Appendix 2.

2. Observed values for the current gain at an anode composed of n-type germanium lie between 1.4 and 1.8. One must suppose that a product of the primary reaction is itself unstable, and decomposes in such a way as to allow electrons to go into the conduction band of the semiconductor. We believe that current multiplication of some such sort as this plays a very important role in other electrolytic interface systems.

3. The initial primary reaction at a germanium cathode is with electrons rather than with holes in the semiconductor. Sometimes this state of affairs persists; sometimes the reaction seems to be replaced, in a time of the order of seconds or minutes, by one involving holes. The current gain is of the order of unity.

4. The surface recombination velocity at the surface of an n-type or p-type germanium sample of the resistivities used, in contact with an electrolyte, is not greater than a few hundred cm/sec.; and it is less when the surface is passing anodic current than cathodic. At the same time we do not exclude the possibility that, at large cathodic current densities, or after a considerable interval of time, the surface recombination velocity, depending on the way in which it is defined, is large. Some peculiar effects have been observed by us in a different experiment from that described here. An attempt was made to measure minority carrier lifetime by exposing a rod of n-type germanium to a cathodic current and studying the decay of photo-conductivity (the Haynes-Hornbeck¹⁵ experiment). The decay curve showed a very sharp initial decline, followed by a horizontal portion, and then a much slower disappearance of remaining carriers. The reason for this is not understood. It is perhaps worth noting here that some time was wasted in searching for a reliable way to determine the surface recombination velocity while the surface was exposed to an electrolyte by such methods as measuring diffusion lengths in filaments. In interpreting such experiments, one must not forget the extra complications arising from current crossing the surface.

5. There are some similarities between the properties of semiconductor-electrolyte interfaces and those of semiconductor-metal junctions. In both cases it is possible to obtain rectification on both n and p-type germanium, with that on n-type being sharper. In both cases there can be current gain. The geometry of a point-contact rectifier is very difficult to analyze quantitatively. We suggest that the techniques discussed in this paper might however prove profitable in understanding the type

of plated metal-semiconductor contact recently described by Schwartz and Walsh¹⁵ and others.¹⁶

6. The rectifying properties of a semiconductor-electrolyte interface may also be described as follows. When n-type germanium is passing anodic current, it is of such a sign as to attract negative ions to the surface; in consequence, the sign of the space-charge region in the surface of the semiconductor must be positive. One might therefore expect that the surface would be p-type. Since the bulk and the surface of the semiconductor now form a p-n junction, across which current is passing in the reverse direction, the current eventually saturates. This description, however, obscures the main point: the current across a junction only saturates when the current from *both* sides is limited by diffusion, and it is again necessary to conclude that electrons cannot easily pass from the anions in the solution into the semiconductor.

7. The relation found experimentally between surface photo-effect and electrode potential is strikingly similar to that reported by Brattain and Bardeen between surface photo-effect and contact potential in the germanium-gas system. Nevertheless, the interpretation we have given appears to be quite different. Let us therefore see how the treatment of the contact potential experiments might apply to the present experiments. In the theoretical discussion of Brattain and Bardeen, the point of departure is that the total surface *charge-density* due to the space-charge and surface states associated with the germanium and to ions adsorbed on the surface, is zero. When the surface is suddenly illuminated, the last contribution does not have time to change: the surface photo-effect may then be calculated on certain assumptions. Now it would seem to be perfectly possible to treat the germanium-electrolyte system in the same way. Any such model must agree with the thermodynamical treatment in the extremes of electrode or contact potential: it is only in the intermediate region that there can be discrepancies. In the paper of Brattain and Bardeen,⁶ where space-charge is neglected, the extent of the intermediate region depends on the number of surface states; in a treatment of Garrett and Brattain,⁷ where surface states are neglected, the extent of the intermediate region is fixed. We have evaded the issue altogether in this paper, by employing semi-empirical expressions for the over-voltage, equations (1) and (6). We have not attempted to describe in detail the problem of the relation between "activation" and current crossing the surface, from which the expressions for over-voltage can be derived, this being the problem in the electrolyte system analogous to that of the relation between the measured contact

potential and the surface potential (the electrostatic potential at the semiconductor surface) in the germanium-gas case. One curious fact may however be pointed out. The theoretical treatment of Garrett and Brattain gives the relation between surface photo-effect and surface potential in the same form as equation (20) of this paper, except that the V^E is replaced by Ψ , the difference between the electrostatic potential at the surface and in the interior, and the coefficient

$$\left(\frac{1}{K_A} + \frac{1}{K_C} \right)$$

is replaced by unity. Now we found the experimental value of

$$\left(\frac{1}{K_A} + \frac{1}{K_C} \right)$$

to be 1.0; it is therefore tempting to apply the theory of Garrett and Brattain to the present case. To do this would be to claim that V^E and Ψ are identical, except for an additive constant, in the region of low current density: that is, all the measured changes in electrode potential occur across the space-charge region, and effectively none across the space-charge region in the electrolyte. Whether such a conclusion is justified must be left for further experiments to decide. In any case it has to be admitted that, since the interpretation of these experiments may be so concisely accomplished by thermodynamical arguments, the role of surface states remains obscure. However, the main deduction of this work — the importance of holes in anodic processes and of electrons in cathodic processes — may furnish a clue towards the understanding of more complicated effects of chemical treatments upon semiconductor surface properties.

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APPENDIX 1

ANALYSIS OF THE THIN SLICE EXPERIMENTS

We start with some remarks about surface recombination velocity. Consider a plane surface bounding n-type germanium; let x be the distance between a point in the germanium and the surface. Let $x = X$ define a plane just sufficiently far into the material that the field E is comparatively small, i.e. such that, in any flow of minority carriers, diffusion predominates over drift. We shall refer to a point in this plane as being "just inside the space-charge region". Experiment shows that the recombination current to the surface depends on the concentration p_1^X of minority carriers at X . The surface recombination velocity v is defined¹⁷ so that

$$(I_p)^{\text{rec.}} = ev(p - p_1^X) \quad (\text{A1})$$

where p is the equilibrium concentration, and $(I_p)^{\text{rec.}}$ is the hole current flowing away from the surface as the net result of surface thermal generation and surface recombination.

Suppose next that current is crossing the surface, in such a way as to tend to change the minority carrier density in the semiconductor. This state of affairs may be described by replacing (A1) by the equation:

$$I_p = I_p' + ev(p - p_1^X) \quad (\text{A2})$$

where I_p' may be considered to be "net hole current flowing into the semiconductor". Notice that, even if one can measure I_p with and without current crossing the surface, equation (A2) does not suffice to determine I_p' experimentally, since we have said nothing as to whether v is or is not also changed by switching on the current. (If, however, we assume that I_p' is uniquely determined by the current crossing the surface, we may vary p_1^X and so determine v . This is what is done in the preceding paper.)

We turn now to the problem of illumination of the surface. Visible light is absorbed in a thickness comparable with that of the surface space-charge region. Let us suppose that the hole current very close to $x = 0$ is still given by equation (A2): what then is the hole current at $x = X$? First notice that X , although large in comparison with atomic dimensions, is (in germanium) very small in comparison with a body diffusion length. Therefore it is sufficient to assume that there is no recombination between 0 and X . Throughout this region, p_1 may vary with distance in a complicated way, and may even be greater than n_1

near the surface; but the continuity equation:¹⁸

$$\frac{\partial p_1}{\partial t} = \frac{1}{e} \operatorname{div} I_p - f(x) \quad (\text{A3})$$

is always satisfied. Here $f(x)$ stands for the rate of creation of holes per unit volume by photo-excitation at $x = X$. $f(x)$ satisfies the condition

$$N = \int_0^\infty f(x) dx \sim \int_0^X f(x) dx \quad (\text{A4})$$

where N is the rate of pair excitation per unit area of surface. In the steady state $\partial p_1 / \partial t = 0$, and for our one-dimensional geometry we have

$$I_p = e \int_0^X f(x) dx + A \quad (\text{A5})$$

But we suppose that, at $x = 0$, I_p is given by equation (A2): therefore

$$(I_p)_x = eN + I_p' + ev(p - p_1^x) \quad (\text{A6})$$

But X has been chosen in such a way that E is negligible in the flow of minority carriers: thus we may write:

$$\left(\frac{dp_1}{dx}\right)_x = -\frac{(I_p)_x}{eD} = -\frac{L + I_p'}{eD} + \frac{v}{D} (p_1^x - p) \quad (\text{A7})$$

We now proceed to use this as the appropriate boundary condition in the solution of the minority carrier flow problem for the thin slice geometry. In this problem we suppose the germanium to be in the form of a thin sheet of thickness t , extending indefinitely in all directions. The electrolyte and alloyed contacts are in the form of two circular areas, of radius r_0 , opposite one another, one on each side of the sheet. Recombination and generation of minority carriers can in principle take place (i) in the body; (ii) at the germanium surface lying further than r_0 from the axis; (iii) at the electrolyte interface; and (iv) at the alloyed interface. If it were not for (ii) the problem would be one-dimensional, and quite easy to solve. The whole problem is of course identical with that of a junction alloyed transistor.

Consider first diffusion to the sides, with a recombination velocity v_0 for the neighboring germanium. Assume as a rough approximation that the hole density is constant across the slice, i.e., is a function only of r , the distance from the axis. Elementary reasoning then leads to the equation:

$$r^2 \frac{d^2 \Delta p}{dr^2} + r \frac{d \Delta p}{dr} - \frac{2v_0}{tD} r^2 \Delta p = 0 \quad (\text{A8})$$

where $\Delta p = p_1 - p$. The solution of this having the property $\Delta p \rightarrow 0$ as $r \rightarrow \infty$ is the Hankel function of order zero:

$$\Delta p = CH_0^{(1)}(ir_0\sqrt{2v_0/tD}) \quad (\text{A9})$$

Let us define a quantity v^* , such that the total flow of minority carriers across the cylinder of radius r_0 is given by:

$$(2\pi r_0 l)ev^*(\Delta p)_{r_0} \quad (\text{A10})$$

From equation (A9) one finds

$$v^* = \frac{D}{L_s} \left[-H_1^{(1)}\left(\frac{ir_0}{L_s}\right) / H_0^{(1)}\left(\frac{ir_0}{L_s}\right) \right] \quad (\text{A11})$$

where L_s is the "sideways diffusion length":

$$L_s = \sqrt{tD/2v_0} \quad (\text{A12})$$

In a practical case L_s is rather smaller than r_0 , and the ratio of the Hankel functions in equation (A11) is not very different from unity. The purpose of the foregoing analysis is to show that, at least in the approximation used, recombination at the outlying free germanium surface may be treated by regarding the surface of the cylinder of radius r_0 as the recombining surface, with a recombination velocity given by equation (A11).

We now use this concept to apply to the case in which the hole density is allowed to vary across the slice, and, as we are now mainly interested in condition for $r < r_0$, we suppose that now the radial variation in p may be neglected. From the diffusion and continuity equations one has:

$$D \frac{d^2 \Delta p}{dx^2} = \left(\frac{2v^*}{r_0} + \frac{1}{\tau} \right) \Delta p \quad (\text{A13})$$

The solution of this is

$$\Delta p = Ae^{x/\lambda} + Be^{-x/\lambda} \quad (\text{A14})$$

where

$$\lambda^2 = D / \left(\frac{1}{\tau} + \frac{2v^*}{r_0} \right) \quad (\text{A15})$$

A and B are determined by the boundary conditions at* the electrolyte surface ($x = 0$) and at the alloyed surface ($x = t$). Let us suppose that the recombination velocities are v_E and v_A , the latter being, pre-

* I.e., "just inside".

sumably, small: and suppose that the hole current across the electrolytic surface (in the sense defined above) is I_p^E , and that across the regrown surface I_p^R : and suppose finally that the electrolyte surface is illuminated, with L/e hole-electron pairs created per second. I_p^E , I_p^R and L are expressed on a unit-area basis. From the boundary conditions (as in equation A7) we have:

$$\begin{aligned} -eD \left. \frac{dp_1}{dx} \right|_0 &= -\frac{eD}{\lambda} (A - B) \\ &= (I_p^E + L) - ev_R(p_1^0 - p) \\ -eD \left. \frac{dp_1}{dx} \right|_t &= -\frac{eD}{\lambda} (Ae^{t/\lambda} - Be^{-t/\lambda}) \\ &= I_p^R + ev_A(p_1^t - p) \end{aligned} \quad (\text{A16})$$

We are interested in p_1^t and p_1^0 . Expanding the exponentials, and performing a certain amount of algebra, one finds:

$$\begin{aligned} \frac{p_1^0}{p_0} &= 1 + \frac{\gamma' I_p^R + (I_p^E + L)}{I_s} \\ \frac{p_1^t}{p_0} &= 1 + \frac{\gamma'' (I_p^E + L) + I_p^R}{I_s} \end{aligned} \quad (\text{A17})$$

where

$$\begin{aligned} \gamma' &\sim 1 - \frac{t^2}{2D\tau} - \left(v^* \frac{t}{r_0} + v_R \right) \frac{t}{D} \\ \gamma'' &\sim 1 - \frac{t^2}{2D\tau} - \left(v^* \frac{t}{r_0} + v_E \right) \frac{t}{D} \\ I_s &= ep \left(\frac{2v^*t}{r_0} + \frac{t}{\tau} + v_R + v_E \right) (1 + \Delta) \end{aligned} \quad (\text{A18})$$

where Δ is small of the order of v^*t/D or a comparable quantity. Equations (17) are identical with equations (8) and (9) in the text.

APPENDIX 2

THERMODYNAMICAL DISCUSSION OF A SEMICONDUCTOR ELECTRODE

First we show how, when the germanium-electrolyte interface is permeable only to holes, the equilibrium electrode potential includes the

electrochemical potential for holes. We follow the notation of Guggenheim¹⁹ and allow μ to stand for a chemical potential of an uncharged species, and for an electrochemical potential of a charged species, both quantities being defined by the equation

$$\mu_i = (\partial G / \partial n_i)_{T, P, n_j} \quad (\text{A19})$$

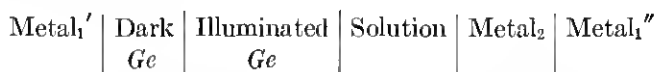
For holes and electrons in germanium

$$\begin{aligned} \mu_p^{ac} &= \varphi_p = \psi + \frac{1}{\beta} \ln \frac{p}{n_i} \\ \mu_n^{ac} &= -\varphi_n = -\psi + \frac{1}{\beta} \ln \frac{n}{n_i} \end{aligned}$$

For germanium under equilibrium conditions, and for a metal under any practically realizable condition,

$$\mu_p + \mu_n = 0 \quad (\text{A20})$$

Now consider the cell:



Suppose that holes are required for the reaction at the germanium solution interface; it is immaterial which is required at the (metal₂ | solution) interface, since equation (A20) is satisfied in metal₂. Let us suppose that the cell reaction is:

$$A - p_{\text{Ill } Ge} = B + n_2 \quad (\text{A21})$$

where A and B denote any chemical or ionic species. We have written the cell reaction in a rather unusual way, to emphasize that, at the same time as one gram-equivalent of A is converted into B , one Faraday of holes is removed from the germanium surface, and one Faraday of electrons removed from metal₂. Let us contemplate the process of taking one electronic charge across the cell, completing the circuit by connecting the cell terminals via a battery of e.m.f. equal to that of the cell. Since this process may be carried out reversibly, and since we have included

electrons and holes as thermodynamic components,

$$\Delta G = 0 \quad (\text{A22})$$

Let us now write down the available thermodynamic relations between the μ 's. To avoid conversion factors, we shall suppose them to be specified in electron volts. We have:

$$\begin{aligned} \mu^A - \mu^B - \mu_{ps}^{Ge} - \mu_{n2} &= 0 \\ \mu_{n2} &= \mu_{n1''} \\ \mu_{p0}^{Ge} &= \mu_{p1'} \\ \mu_{p1'} &= -\mu_{n1'} \end{aligned} \quad (\text{A23})$$

where μ_{ps}^{Ge} and μ_{p0}^{Ge} refer respectively to the surface (illuminated) and equilibrium (dark) parts of the germanium. Then the measured voltage between the right and left hand sides of the cell is

$$\begin{aligned} V &= \mu_{n1'} - \mu_{n1''} \\ &= \mu_B - \mu_A + (\mu_{ps}^{Ge} - \mu_{p0}^{Ge}) \end{aligned} \quad (\text{A24})$$

Thus, so long as the potentials of the reacting components in the solution remain constant,

$$V = V^0 + \frac{1}{\beta} \ell n \frac{p_1}{p} \quad (\text{A25})$$

The same argument may be repeated for the case that the germanium-electrolyte interface is permeable only to electrons, and gives

$$V = V^{0'} - \frac{1}{\beta} \ell n \frac{n_1}{n} \quad (\text{A26})$$

We now evaluate the magnitude of the photo-voltage for these two extreme conditions:

$$\begin{aligned} \left(\frac{\partial V}{\partial L} \right)_I &= \frac{\partial}{\partial L} \left(\varphi_{ps} - \varphi_0 \right) && \text{anode} \\ \left(\frac{\partial V}{\partial L} \right)_I &= \frac{\partial}{\partial L} \left(\varphi_{ns} - \varphi_0 \right) && \text{cathode} \end{aligned} \quad (\text{A27})$$

If the material is n-type, and if the mobility of electrons and holes were equal, it may be shown⁷ that

$$\begin{aligned}
\left(\frac{\partial}{\partial L}\right)_I (\varphi_{ps} - \varphi_0) &= \frac{1}{\beta} \frac{1}{I_s + L + I_p} = \frac{1}{\beta I_s} \frac{p}{p_1} \\
\left(\frac{\partial}{\partial L}\right)_I (\varphi_{ns} - \varphi_0) &= -\left(\frac{p}{n}\right) \frac{1}{\beta} \frac{1}{I_s + (p/n)(L + I_p)} \\
&= -\frac{p}{n} \frac{1}{\beta I_s} \frac{n}{n_1}
\end{aligned} \tag{A28}$$

with the notation used in the text. Because the mobilities are not equal, there is an additional term,²⁰ too small to affect the upper equation, but of the same magnitude as the lower:

$$\frac{d\delta V_i}{dL} = +\left(\frac{p}{n}\right) \frac{1}{\beta} \left(\frac{b-1}{b}\right) \frac{1}{I_s + \frac{p}{n} \frac{b+1}{b} (L + I_p)} \tag{A29}$$

Allowing for this, and approximating equations (A28) and (A29) for the case that L and I_p are small in comparison with I_s ,

$$\begin{aligned}
\left(\frac{\partial V}{\partial L}\right)_I &= \frac{1}{\beta I_s} \quad \text{anode} \\
\left(\frac{\partial V}{\partial L}\right)_I &= -\frac{p}{nb} \frac{1}{\beta I_s} \quad \text{cathode}
\end{aligned} \tag{A30}$$

In a similar way, it may be shown for p-type material that

$$\begin{aligned}
\left(\frac{\partial V}{\partial L}\right)_I &= \frac{nb}{p} \frac{1}{\beta I_s} \quad \text{anode} \\
\left(\frac{\partial V}{\partial L}\right)_I &= -\frac{1}{\beta I_s} \quad \text{cathode}
\end{aligned} \tag{A31}$$

under the same conditions. (I_s now means the *electron* saturation current.) Notice from equation (28) that the cathode photo-effect on n-type (and the anode photo-effect on p-type) is relatively insensitive to the magnitude of L and I_p . This is well shown in Fig. 6.

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